THE H-THEOREM FOR THE DISCRETE QUANTUM KINETIC EQUATIONS AND FOR ITS GENERALIZATIONS

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The *H*-theorem for generalization of equations of chemical kinetics is proved. Important physical examples of such generalization: the discrete velocity models of the quantum kinetic equations (of the Uehling–Uhlenbeck equations) and the quantum Markoff process (the quantum random walk), are considered. The coincidence of time means with the Boltzmann extremals for Liouville equation's type is proved.

It is shown, that «the Boltzmann procedure» of variation of entropy, leads to «the Boltzmann formula», [1] is applicable to both the Boltzmann equation and its discrete velocity models, as well as to the equation of continuity, and in the finite dimensional case for the Markoff processes and its non-linear generalizations of chemical kinetics' type.

Let U is a linear operator in Hilbert space X, and the norm of U is less than or equal to one. Then the theorem, called stochastic ergodic theorem (F. Riesz, see [2]), is valid. For each z of the X time means

$$P_{nm}(z) = (n-m)^{-1} \sum_{k=m}^{n-1} U^k z$$

converge strongly to an element $P^C = P^C(z)$ – the Cesaro average, when $n-m$ tends to infinity.

We define the Boltzmann extremal as an element P^B, where the entropy reaches its conditional maximum. More precisely, we define a set of linear conservation laws $I \subset X$, $u \in I$, if

$$(Ux,u) = (x,u)$$

For all $x \in X$. Consider $S(x)$ – a strictly concave (convex upwards) functional, not decreasing under the action U: $S(Ux) \geq S(x)$ (it is an analog of entropy). Let X_z is a set of $x \in X$ with the same constants of the linear conservation laws as for z: $X_z = \{x \in X, (x-z,u) = 0 \text{ for all } u \in I\}$. Consider the conditional extremum problem: find out where $\sup S(x)$ is achieved on condition that $x \in X_z$. Argument of functional $S(x)$, that yields this conditional extremum, call $P^B(z)$ = (the Boltzmann extremal).

Theorem. Let S is defined on X_z, and if X_z is unrestricted, then $\lim\limits_{\substack{\|x\|\to+\infty \\ x\in X_z}} S(x) = -\infty$.

Then:

1) the solution of this conditional extremum problem exists into X_z and is unique;

2) the Cesaro averages coincide with the Boltzmann extremals:

$$P^C(z) = P^B(z).$$

Example. The Liouville equation for discrete time for the M. Katz model [3, 4].

Consider the circle and n equally spaced points on it (vertices of a regular inscribed polygon). Note some of their number: m vertices. The set of them we label by S. In each of the n points put the black or white ball. During each time unit, each ball moves one step counter-clockwise with the following condition: the ball going out from a point of the set S changes its color. If the point does not belong to S, the ball leaving it retains its color.

We introduce the following notation. We number the points counter-clockwise from 1 to n; let p is a number between 1 and n. $\varepsilon_p = -1$, if $p \in S$; $\varepsilon_p = +1$, if $p \notin S$. $\eta_p(t) = +1$, if at the moment t the ball in the point p is black; $\eta_p(t) = -1$, if at the moment t the ball in the point p is white. Directly from the model it is obtained:

$$\begin{aligned} &\eta_1(t+1) = \varepsilon_n \eta_n(t), \\ &\eta_p(t+1) = \varepsilon_{p-1}\eta_{p-1}(t),\ p = 2,3,\ldots,n. \end{aligned} \tag{1}$$

We write the system (1) in vector form:

$$\boldsymbol{\eta}(t+1) = \hat{\mathbf{T}}\boldsymbol{\eta}(t), \tag{2}$$

where $\boldsymbol{\eta}(t) = (\eta_1(t), \eta_2(t), \ldots, \eta_n(t))^T$,

$$\hat{\mathbf{T}} = \begin{pmatrix} 0 & 0 & 0 & \ldots & 0 & \varepsilon_n \\ \varepsilon_1 & 0 & 0 & \ldots & 0 & 0 \\ 0 & \varepsilon_2 & 0 & \ldots & 0 & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & 0 & \ldots & 0 & 0 \\ 0 & 0 & 0 & \ldots & \varepsilon_{n-1} & 0 \end{pmatrix}.$$

The Liouville equation for (1) (and (2)) has the form:

$$f(\eta_1, \eta_2, \ldots, \eta_n; t+1) = f(\varepsilon_1\eta_2, \varepsilon_2\eta_3, \ldots, \varepsilon_n\eta_1; t). \tag{3}$$

For the Liouville equation (3) there is always the law of conservation of all states of the balls – vectors $\boldsymbol{\eta}$: $\sum\limits_{\boldsymbol{\eta}} f(\boldsymbol{\eta}; t) = const$, where summation is over all possible vectors $\boldsymbol{\eta}$ (the number

of them is equal to 2^n). Therefore, the entropy $\sum_{\boldsymbol{\eta}} f(\boldsymbol{\eta};t)\ln f(\boldsymbol{\eta};t)$ is bounded, if the constants of the linear conservation laws are fixed. It conserves on the solutions of (4). So the condition of the theorem is satisfied and time mean coincides with the Boltzmann extremal, although each system returns to its original state after a time $2n$ – each point changes its color after $2n$ steps an even number of times: $2m$.

The Boltzmann extremal and the Cesaro average are determined by the linear conservation laws. Let us find out what they are and how many. As we have noted, a system after $2n$ steps returns to its original state. It may be that she repeatedly returned to its original state for the same period of time. At the same time it may be that it repeatedly returned to its original state for the same period of time. Therefore, the system, going through different states one at a time, will return at the first time in its original state after a number of steps, which is a divisor of the number $2n$. The linear conservation law: $f(\boldsymbol{\eta}^0;t)+f(\boldsymbol{\eta}^1;t)+\ldots+f(\boldsymbol{\eta}^{2n-1};t)=const$, corresponds to that the system at first time returns to its original state after k steps: $\boldsymbol{\eta}^0\to\boldsymbol{\eta}^1\to\ldots\to\boldsymbol{\eta}^{k-1}\to\boldsymbol{\eta}^0$. Thus, the problem boils down to counting the number of solutions of the equation $\boldsymbol{\eta}=\hat{\mathbf{T}}^k\boldsymbol{\eta}$: there are no solutions for odd m and $k/НОД(n,k)$, and in other cases the number of them is $2^{НОД(n,k)}$.

Subtract from the number of solutions of equation $\boldsymbol{\eta}=\hat{\mathbf{T}}^k\boldsymbol{\eta}$ for each of the divisors of k the number of states such that after the number of steps, equal to this divisor, the system at first time returns to its original state. If this number we divide by k, then we get a number of conservation laws corresponding to the fact that after k steps the system returns to its original state the first time.

Since the writing of the general formula is too cumbersome, then we write the answer for the example when $n=p_2^{\,2}\cdot p_3$, then for even m the number of the conservation laws число законов сохранения is equal to

$$\frac{2}{1}+\frac{2^{p_2}-2}{p_2}+\frac{2^{p_3}-2}{p_3}+\frac{2^{p_2^{\,2}}-\left(2^{p_2}-2\right)-2}{p_2^{\,2}}+$$

$$+\frac{2^{p_2p_3}-\left(2^{p_2}-2\right)-\left(2^{p_3}-2\right)-2}{p_2p_3}+\frac{2^{p_2^{\,2}p_3}-2^{p_2p_3}-2^{p_2^{\,2}}+2^{p_2}}{p_2^{\,2}p_3}=$$

$$=2+\frac{2^{p_2}-2}{p_2}+\frac{2^{p_3}-2}{p_3}+\frac{2^{p_2^{\,2}}-2^{p_2}}{p_2^{\,2}}+\frac{2^{p_2p_3}-2^{p_2}-2^{p_3}+2}{p_2p_3}+\frac{2^{p_2^{\,2}p_3}-2^{p_2p_3}-2^{p_2^{\,2}}+2^{p_2}}{p_2^{\,2}p_3},$$

and for odd m:

$$\frac{2}{2}+\frac{2^{p_2}-2}{2p_2}+\frac{2^{p_3}-2}{2p_3}+\frac{2^{p_2^{\,2}}-2^{p_2}}{2p_2^{\,2}}+\frac{2^{p_2p_3}-2^{p_2}-2^{p_3}+2}{2p_2p_3}+\frac{2^{p_2^{\,2}p_3}-2^{p_2p_3}-2^{p_2^{\,2}}+2^{p_2}}{2p_2^{\,2}p_3}.$$

Let consider the system of equations:

$$\frac{df_i}{dt}=\sum_{(\boldsymbol{\alpha},\boldsymbol{\beta})\in\Im}(\beta_i-\alpha_i)\sigma_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}(\mathbf{f})\tilde{K}_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}e^{\left(\boldsymbol{\alpha},\nabla G(\mathbf{f})\right)},\ i=1,2,\ldots,n, \tag{4}$$

where $\boldsymbol{\alpha}=(\alpha_1,\alpha_2,\ldots,\alpha_n)$ and $\boldsymbol{\beta}=(\beta_1,\beta_2,\ldots,\beta_n)$ – vectors with integer-valued nonnegative components, and summation leads on certain finite set $\Im$ of multiindexes $(\boldsymbol{\alpha},\boldsymbol{\beta})$, symmetric under permutations $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$; $\sigma_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}(\mathbf{f})$, $G(\mathbf{f})$ – given functions from $\mathbf{f}=(f_1,f_2,\ldots,f_n)$, $\sigma_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}(\mathbf{f})=\sigma_{\boldsymbol{\alpha}}^{\boldsymbol{\beta}}(\mathbf{f})>0$; $\tilde{K}_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}\geq 0$.

If $\sigma_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}(\mathbf{f})$ is independent on $\mathbf{f}$, then we have the system:

$$\frac{df_i}{dt}=\sum_{(\boldsymbol{\alpha},\boldsymbol{\beta})\in\Im}(\beta_i-\alpha_i)K_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}e^{\left(\boldsymbol{\alpha},\nabla G(\mathbf{f})\right)},\ i=1,2,\ldots,n, \tag{5}$$

where $K_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}=\sigma_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}\tilde{K}_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}$.

If in (5) $\frac{\partial G(\mathbf{f})}{\partial f_i}=\ln f_i$, then we have chemical kinetics' system of equations [5]. The principle of detailed balance and the condition of dynamic equilibrium are considered in chemical kinetics [5, 6]. The latter is also named the principle of unitarity or the Stuckelberg–Batishcheva–Pirogov condition [7, 8, 9].

For the system (4) the following generalization of the principle of detailed balance can be formulated. Let vector $\boldsymbol{\xi}$ exists such, that for all reactions $(\boldsymbol{\alpha},\boldsymbol{\beta})\in\Im$ the condition:

$$\tilde{K}_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}e^{\left(\boldsymbol{\alpha},\nabla G(\boldsymbol{\xi})\right)}=\tilde{K}_{\boldsymbol{\alpha}}^{\boldsymbol{\beta}}e^{\left(\boldsymbol{\beta},\nabla G(\boldsymbol{\xi})\right)}. \tag{6}$$

is fulfilled.

Let define the generalization of the Stuckelberg–Batishcheva–Pirogov principle on the case of systems (5) in the following way. Let vector $\boldsymbol{\xi}$ exists such, that it is a solution of the system of equations:

$$\sum_{\boldsymbol{\beta}}K_{\boldsymbol{\beta}}^{\boldsymbol{\alpha}}e^{\left(\boldsymbol{\alpha},\nabla G(\boldsymbol{\xi})\right)}=\sum_{\boldsymbol{\beta}}K_{\boldsymbol{\alpha}}^{\boldsymbol{\beta}}e^{\left(\boldsymbol{\beta},\nabla G(\boldsymbol{\xi})\right)}, \tag{7}$$

here $\boldsymbol{\alpha}$ is such, that $(\boldsymbol{\alpha},\boldsymbol{\beta})\in\Im$ with some $\boldsymbol{\beta}$.

We prove the *H*-theorem for systems (4) on conditions (6) and for systems (5) on conditions (7), and the *H*-function (a functional of type of entropy, decreasing on non-stationary solutions) is defined by the equation: $H(\mathbf{f})=G(\mathbf{f})-(\nabla G(\boldsymbol{\xi}),\mathbf{f})$. The *H*-theorem for

the symmetrical case: $\sigma_{\beta}^{\alpha}(\mathbf{f})\widetilde{K}_{\beta}^{\alpha} = \sigma_{\alpha}^{\beta}(\mathbf{f})\widetilde{K}_{\alpha}^{\beta}$, was considered [6].

Example. Random walk with two states and its generalizations.

Markoff process with two states is described by the system of two equations:

$$\begin{cases} \dfrac{df_1}{dt} = K_1^2 f_2 - K_2^1 f_1, \\ \dfrac{df_2}{dt} = K_2^1 f_1 - K_1^2 f_2, \end{cases} \tag{8}$$

quantum random walk with two states – by the system:

$$\begin{cases} \dfrac{df_1}{dt} = K_1^2 f_2(1+\theta f_1) - K_2^1 f_1(1+\theta f_2), \\ \dfrac{df_2}{dt} = K_2^1 f_1(1+\theta f_2) - K_1^2 f_2(1+\theta f_1), \end{cases} \tag{9}$$

and their generalization – by the system:

$$\begin{cases} \dfrac{df_1}{dt} = \sigma(\mathbf{f})\left(K_1^2 \exp\left(\dfrac{\partial G(\mathbf{f})}{\partial f_2} \right) - K_2^1 \exp\left(\dfrac{\partial G(\mathbf{f})}{\partial f_1} \right) \right), \\ \dfrac{df_2}{dt} = \sigma(\mathbf{f})\left(K_2^1 \exp\left(\dfrac{\partial G(\mathbf{f})}{\partial f_1} \right) - K_1^2 \exp\left(\dfrac{\partial G(\mathbf{f})}{\partial f_2} \right) \right). \end{cases}$$

The system (8) represents a system of equations of chemical kinetics with one reaction of the form $S_1 \overset{K_2^1}{\to} S_2$ and with return reaction to it $S_2 \overset{K_1^2}{\to} S_1$. While in the asymmetric case the system (9) is not a system of equations of chemical kinetics. The generalization of the condition of detailed balance, proposed in present work, is formulated for this example in this way: there is a vector $\boldsymbol{\xi} = (\xi_1, \xi_2)$ such that $K_1^2 \xi_2/(1+\theta\xi_1) = K_2^1 \xi_1/(1+\theta\xi_2)$.

Nevertheless the problem of construction of the *H*-function (that is decreasing functional with the proof of the *H*-theorem) for the quantum random walks, for which the generalization of the principle of detailed balance (6) is not fulfilled, remains open.

It is considered a new form of the H-theorem in researches of H. Poincare [10], V.V. Kozlov [4] and D.V. Treshchev [11]. It is valid for the Liouville equation and for its generalizations. The concept of the Boltzmann extremal works there also: we prove, that time means (the Cesaro averages) coincide with the Boltzmann extremals. And that makes the concept of the Boltzmann extremal generally mathematical and fundamental both as search method of stationary solutions of wide class of equations both linear of Liouville equation's type and nonlinear, and as broad generalization of the concept of entropy.

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References

1. Boltzmann L. Weitere Studien über das Wärmegleichgewicht unter Gasmolekülen. Wien: Akad. Sitzungsber, 1872. Bd. 66. S. 275–370.
2. Riesz F., Szkefalvi-Nagy B. Lectures on functional analysis. Moscow: Mir, 1979 (in Russian).
3. Katz M. Several probability problems of physics and mathematics. Moscow: Nauka, 1967 (in Russian).
4. Kozlov V.V. Thermal equilibrium in the sense of Gibbs and Poincare. Moscow–Izhevsk: Institute of Computer Science, 2002 (in Russian).
5. Vol'pert A.I., Hudjaev S.I. Analysis in classes of discontinuous functions and equations of mathematical physics. Moscow: Nauka, 1975 (in Russian).
6. Vedenyapin V.V. The kinetic theory by Maxwell, Boltzmann and Vlasov. Moscow: publishing house of the Moscow state regional university, 2005 (in Russian).
7. Lifschitz E.M., Pitaevskii L.P. The physical kinetics. Series: " The theoretical physics", vol. X. Moscow: Nauka, 1979 (in Russian).
8. Batishcheva Ya.G., Vedenyapin V.V. The 2-nd law of thermodynamics for chemical kinetics // Matem. Mod. 2005. 17:8, 106–110 (in Russian).
9. Malyshev V.A., Pirogov S.A. Reversibility and irreversibility in stochastic chemical kinetics // Russian Math. Surveys. 2008. 63:1, 1–34.
10. Poincare H. Remarks on kinetic theory of gases. // Poincare H. Selected works. Vol. 3. Moscow, 1974 (in Russian).
11. Kozlov V.V., Treshchev D.V. Weak convergence of solutions of the Liouville equation for nonlinear Hamiltonian systems // Theoret. and Math. Phys., 134:3 (2003), 339–350.